Message

From: Washington, John [/O=EXCHANGELABS/OU=EXCHANGE ADMINISTRATIVE GROUP (FYDIBOHF23SPDLT)/CN=RECIPIENTS/CN=FDC3E8CE9F1D45C4894881FF420CA104-WASHINGTON, JOHN]
Sent: 12/6/2018 3:22:03 PM
To: Strynar, Mark [/o=ExchangeLabs/ou=Exchange Administrative Group (FYDIBOHF23SPDLT)/cn=Recipients/cn=5a9910d5b38e471497bd875fd329a20a-Strynar, Mark]; Post, Gloria [Gloria.Post@dep.nj.gov]; Lindstrom, Andrew [/o=ExchangeLabs/ou=Exchange Administrative Group (FYDIBOHF23SPDLT)/cn=Recipients/cn=04bf7cf26aa44ce29763fbc1c1b2338e-Lindstrom, Andrew]
CC: McCord, James [/o=ExchangeLabs/ou=Exchange Administrative Group (FYDIBOHF23SPDLT)/cn=Recipients/cn=McCord, James]; Williams, Antony [/o=ExchangeLabs/ou=Exchange Administrative Group (FYDIBOHF23SPDLT)/cn=Recipients/cn=959e02b5a0da419a9d749469dfe05c34-Williams, A]; Richard, Ann [/o=ExchangeLabs/ou=Exchange Administrative Group (FYDIBOHF23SPDLT)/cn=Recipients/cn=8980b96d55ae4a268db3cd9bc3e5a865-Richard, Ann]
Subject: Re: More info from Z Wang RE: Question about product shown in Zhang et al. (2013)

Nice work Gloria!

With it being a large molecule, I will look for it in the soil extracts as well.

It was great to see you again and meet all the NJ DEP scientists in person.

Thanks for your hospitality,
John

From: Strynar, Mark
Sent: Thursday, December 6, 2018 9:31:57 AM
To: Post, Gloria; Lindstrom, Andrew; Washington, John
Cc: McCord, James; Williams, Antony; Richard, Ann
Subject: RE: More info from Z Wang RE: Question about product shown in Zhang et al. (2013)

Here is the PDF of the EFSA doc. James and I will look for it asap. The Chemicals dashboard link has no structure (shown on section 4.1) of attached document.

https://comptox.epa.gov/dashboard/dsstoxdb/results?search=DTXSID00882626

Mark

From: Post, Gloria <Gloria.Post@dep.nj.gov>
Sent: Thursday, December 06, 2018 7:36 AM
To: Strynar, Mark <strynar.mark@epa.gov>; Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>; Washington, John <Washington.John@epa.gov>
Subject: More info from Z Wang RE: Question about product shown in Zhang et al. (2013)

FYI - see my question and his response below.

He is very knowledgeable and helpful.

Also - I am not answering his question about what you are finding in your study with NJDEP since this is not yet public information

Thanks
Gloria

From: Wang Zhanyun (IfU, ESD) <zhanyun.wang@ifu.baug.ethz.ch>
Sent: Thursday, December 6, 2018 4:10:09 AM
To: Post, Gloria
Subject: [EXTERNAL] Re: One more question RE: Question about product shown in Zhang et al. (2013)

Dear Gloria,

That's interesting. I have to say that I didn't read it carefully. It's possible that Solvay may have used both compounds in its PVDF production. The reason why they need so much compound XIII (the one mentioned in the EFSA opinion) may be its less stable, so they would need high amounts (although there isn't any information on the degradability of this compound in the public domain). It may have been used to substitute the high amounts of the other compound, which is a short-chain homologue of Solvay's own PFPE products (probably a byproduct from Solvay's own PFPE production). There was also similar patents to use PFHxA to substitute PFOA in the PTFE production, so one may use only much less PFOA in the presence of PFHxA. Of course it's just an example in the patent, and real production conditions may be quite different from the example, but still within the overall claim of the patent. I think Andy does found the other compound also from the wastewater from Solvay's site, right?

Best regards,
Zhanyun

On 5 Dec 2018, at 17:01, Post, Gloria <Gloria.Post@dep.nj.gov> wrote:

Zhanyun,

I have one more question, probably since I am a toxicologist not a chemist!

Example 10 that you pointed me to says:

> Polymerization Example 10 Manufacture of a PVDF Latex in the Presence of Mixture of Surfactant
> A reactor having an inner volume of 7.57 l was charged with 5241 g of deionized water, 134 g of 10% w/w aqueous solution of compound XIII (X_a=NH_4), and 5.4 mg of dicarboxylic perfluoropolyether acid ammonium salt of formula: $X_aOOC—CF_2O—(CF_2O)_n(CF_2CF_2O)_m—CF_2—COOX_a$ (X_a=NH_4, n, m being such that average molecular weight is 1800),

The substance highlighted in green was used in very small amounts compared to Compound XIII. Do you know anything about this? It seems like it would be a large molecule, with average MW of 1800.

Thanks,
GLoria

From: Wang Zhanyun (IfU, ESD) <zhanyun.wang@ifu.baug.ethz.ch>
Sent: Wednesday, December 05, 2018 9:36 AM
To: Post, Gloria <Gloria.Post@dep.nj.gov>
Subject: [EXTERNAL] Re: Question about product shown in Zhang et al. (2013)

You are welcome!

> On 5 Dec 2018, at 14:58, Post, Gloria <Gloria.Post@dep.nj.gov> wrote:
>
> Thanks so much. This is very helpful!!!
>
> Gloria B. Post, Ph.D., DABT
> Research Scientist
>
> Division of Science, Research, and Environmental Health
> New Jersey Department of Environmental Protection
> Mail Code 428-01, PO Box 420
> Trenton, NJ 08625-0420
>
> Telephone: (609) 292-8497
> Fax: (609) 292-7340

From: Wang Zhanyun (IfU, ESD) <zhanyun.wang@ifu.baug.ethz.ch>
Sent: Wednesday, December 5, 2018 8:57:15 AM
To: Post, Gloria
Subject: [EXTERNAL] Re: Question about product shown in Zhang et al. (2013)

Dear Gloria,

The substance is registered under REACH by Miteni in 2012 (which recently claimed bankruptcy) and Solvay in 2018, so I think it's a Solvay product. I know (almost) for sure that this substance has been used by Solvay as an emulsifier in PTFE production (as I talked to one Solvay person at a workshop and they have a couple of patents on this). I've also found a patent from Solvay using this substance in the production of PVDF (https://patents.google.com/patent/US20140228531?oq=hod+for+manufacturing+fluoropolymers+in+the+presence+of+cyclic+fluorosurfactants+with+low+bioaccumulation%2fbiopersistence, see example 10). So I would say it's likely that this substance has been used in the PVDF production as well.

Best regards,
Zhanyun

> On 5 Dec 2018, at 14:23, Post, Gloria <Gloria.Post@dep.nj.gov> wrote:
>
> Dear Zhanyun,
>
> Thank you so much for your very helpful and quick response to my question.

In regard to use of emulsifiers in fluoropolymer production, the EFSA document you sent mentions the use of 2-[(5-methoxy-1,3-dioxolan-4-yl)oxy]}, ammonium salt () "during the polymerization process of fluoropolymers such as tetrafluoroethylene homopolymer **and others**."

Solvay produces Kynar (polyvinylidene fluoride; PVDF) in a facility located in our state, New Jersey. Solvay previously used Surflon S-111 as an emulsifier in the production of PVDF at its New Jersey facility. This process is described in the Supplementary Information of Prevedouros et al. (2006) https://pubs.acs.org/doi/suppl/10.1021/es0512475/suppl_file/es0512475.pdf .

As you probably know, Surflon S-111 is a technical mixture consisting primarily of PFNA, with smaller percentages of C11, C13, and other PFAAs. See Tables copied from Supplementary Information of Prevedouros et al. (2006) below.

Solvay stopped using Surflon S-111 at its New Jersey facility in 2010 as part of the Voluntary Stewardship Agreement of major manufacturers with USEPA to end use of PFOA, its precursors, and higher homologues (including PFNA and longer chain PFAAs). It is our understanding that Solvay continues to manufacture PVDF at its New Jersey facility, and that replacement(s) for the phased-out long-chain PFAAs are now being used as emulsifiers.

Do you know if the chemical discussed in the EFSA document (CAS No 1190931-27-1) is a Solvay product, and/or if it is used by Solvay as an emulsifier in fluoropolymer (i.e. PVDF) production?

Any information that you have about these questions would be very much appreciated.

Best regards,
Gloria

COPIED FROM SUPPLEMENTARY INFORMATION IN PREVEDOUROS ET AL. (2006):

<pastedImage.png>

<pastedImage.png>

From: Wang Zhanyun (IfU, ESD) <zhanyun.wang@ifu.baug.ethz.ch>
Sent: Wednesday, December 5, 2018 4:55 AM
To: Post, Gloria
Subject: [EXTERNAL] Re: Question about product shown in Zhang et al. (2013)

Dear Gloria,

thanks for your email. Unfortunately, I don't have much information on this substance. But I think this substance mixture is manufactured by Solvay themselves, as Bob from Dupont told me once that all major fluoropolymer manufacturers (Daikin, 3M, Chemours, Asahi and Solvay) are now using their own emulsifier and I've found a patent from Solvay (formerly Ausimont) showing a similar structure, see Structure 3 (https://patents.google.com/patent/EP0315078A2/en). It is likely that this substance mixtures is a short-chain homologue of the perfluoropolyethers produced by Solvay (Fomblin, Solvera, Galden or Fluorolink), similarly to GenX is a short-chain homologue impurity produced during the production of Krytox. I don't know if it's possible to purchase this substance mixture … Andy from US EPA recently told me that they've detected this substance mixture in the environment. Perhaps he would have some reference standards or know how to get this product.

In addition, Solvay have likely already changed to another emulsifier in their fluoropolymer production: https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/j.efsa.2014.3718

Hope this helps. Should you have any other questions, please do not hesitate to let me know. Have a good day!

Best regards,
Zhanyun

> On 4 Dec 2018, at 22:44, Post, Gloria <Gloria.Post@dep.nj.gov> wrote:
>
> Dear Zhanyun,
>
> I have a question that you may be able to help with. Do you have any information on the product labeled as "Solvay's product (CAS No. 329238-24-6)" in Figure 1 of your 2013 paper? (Please see attached scanned page.)
>
> Do you know whether Solvay manufactures this product or purchases it from someone else? Do you know if it is

possible to purchase or otherwise obtain this product (or any of its component congeners)?

This information, and any other information that you may have about this product, would be greatly appreciated.

Best regards,
Gloria

Gloria B. Post, Ph.D., DABT
Research Scientist

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<Wang et al 2013 figure 1.pdf>